

Scientific registration number: 1773  
Symposium number: 5  
Presentation: poster

## Anion transport in a fine-textured Ultisol in Costa Rica

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### **Abstract**

In the humid tropics, there is a high potential for appreciable losses of mobile nutrients such as nitrates from the root zone due to intense leaching. A dye tracer study and column displacement experiments were conducted to characterize and quantify the important physical and chemical mechanisms governing the transport of anionic tracers in an Ultisol in southern Costa Rica. Displacement experiments demonstrated that adsorption caused bromide to move at a slower rate than water in the subsoil. At high pore water velocities, anion adsorption was not in equilibrium with bulk solution concentrations. The dye tracer study shows that significant bypassing of water and dye occurred in the surface horizon under unsaturated, transient flow conditions.

### **Introduction**

The ability to describe field soil water and solute transport is important for understanding and mitigating a wide range of agricultural and environmental problems. In the humid tropics there is a high potential for appreciable losses of mobile nutrients such as nitrate from the root zone due to intense leaching (Arora and Juo, 1982; Bornemisza, 1982; van der Kruijs et al., 1988; Poss and Saragoni, 1992). Despite significant leaching losses of applied N in Costa Rica (Martinez, et al., 1987), detailed evaluations of transport properties of these soils are lacking. This hampers the identification of important transport mechanisms of solute movement and the identification of management practices which may promote efficient use of soil amendments.

The principal mechanisms that may influence anion transport in acid soils of the tropics other than the amount of infiltrated rainfall includes anion adsorption and physical nonequilibrium. A small amount of anion exchange capacity normally associated with soils containing significant amounts of variable charge minerals (Parfitt, 1980) will slow the movement of nonspecifically adsorbed anions such as  $\text{NO}_3^-$ ,  $\text{Br}^-$ , and  $\text{Cl}^-$ . The retarded movement of anions relative to water has been demonstrated in numerous acid soils of tropical regions (Wong et al., 1990). Physical nonequilibrium or, equivalently, bypass flow describes a phenomenon whereby solution concentrations within two or more soil regions are not at local equilibrium due to slow advective and/or diffusive exchanges between these regions. This can result in an apparent nonequilibrium of adsorbed concentration with respect to solution concentrations when the solute velocities of the two regions are not equivalent. Bypass flow is believed to be responsible for the early breakthrough and tailing associated with displacement experiments in structured soils. Much of the physical evidence for the occurrence of bypass flow in soils is descriptive, such as the use of visible dye

tracers. However, column displacement studies (e.g. Trojan and Linden, 1992) have shown that bypass flow can significantly influence transport rates at or near saturation. The practical significance of anion adsorption and bypass flow is that they can retard leaching so that plants and microorganisms have additional time to immobilize  $\text{NO}_3^-$ -N thereby further slowing the rate of nitrogen loss from the system.

The objective of this research was to characterize the important physical and chemical mechanisms governing the transport of anion tracers in an Ultisol located in southern Costa Rica. Column displacement studies were carried out using intact soil cores to identify transport processes operative under unsaturated, steady-state flow conditions over a range of mean pore water velocities. In addition, a dye tracer study was conducted in small field plots to characterize the spatial pattern of water flow.

## Materials and Methods

The study was conducted in southern Costa Rica on fine textured Ultisols (very fine, kaolinitic, isohyperthermic, Oxyaquic Hapludult) in a two ha study site. This site has an average slope of 20% and a mean annual precipitation of approximately 3000 mm. The site has been managed under a no-till bean-corn rotation for ten years.

In laboratory studies, batch methods were used to obtain adsorption isotherms for  $\text{Br}^-$ ,  $\text{NO}_3^-$ , and Brilliant Blue FCF dye. Concentration ranges of Brilliant blue FCF dye and  $\text{Br}^-$  match those ranges used in the field and columns respectively. Suspensions were allowed to equilibrate for 20 hours at room temperature and centrifuged down to collect the supernatant. For  $\text{Br}^-$  and  $\text{NO}_3^-$  adsorption, the ionic strength was maintained at 0.015 with calcium chloride. Batch adsorption measurements of Brilliant Blue FCF were made using a background concentration of 0.015 M NaCl. Bromide and  $\text{NO}_3^-$  concentrations were measured using an ion-selective electrode whereas dye concentrations were measured using a colorimeter at a wavelength of 630 nm.

Undisturbed soil columns were collected in the field at depths of 0 to 15 cm, 20 to 40 cm, 42 to 57 cm, and 57 to 77 cm corresponding to the Ap/AB, Bt1, Bt2 and Bt3 horizons respectively. Cylindrical soil columns (10.1 cm i.d.) were isolated by incrementally forcing a beveled cutting edge coupled to a polyvinyl chloride pipe over a previously carved pedestal of soil. Excess soil material at the bottom and top of the cylinders was trimmed flush and caps were secured to the ends to permit transport to the laboratory in Costa Rica. Oriented thin sections were prepared from air dry, undisturbed clods impregnated with a polyester resin under a vacuum.

The bottom and top of each column was fitted with fritted glass plates with bubbling pressure heads ranging from -40 to -52 cm  $\text{H}_2\text{O}$ . Displacement experiments were conducted at tensions of -1 to 14 cm  $\text{H}_2\text{O}$  (-1.0 to 13.7 mbars) under a unit hydraulic gradient. Once columns were saturated with 5 mM  $\text{CaCl}_2$ , displacement experiments were conducted at selected pressure heads using 5 mM  $\text{CaBr}_2$  as the influent solution. The bromide tracer was injected continuously only after a steady state flux of 5 mM  $\text{CaCl}_2$  had been established. Bromide concentrations in the effluent solution were measured using an ion-selective electrode. On completion of each displacement experiment, the columns were weighed to allow the determination of water content. The advective-dispersive equation and a dual-porosity model (e.g. Gerke and van Genuchten, 1993) were fitted to dimensionless effluent concentrations using nonlinear, least-squares parameter optimization.

The dye study was carried out in the field during the dry season on twelve plots at three field locations within the site. Within each field location four 1.2 x 1.2 m subplots were established to

examine four experimental treatments: (1) dye application to soil with residue intact and no pre-wetting, (2) dye application to a pre-wetted soil with residue intact (3) dye application to a pre-wetted soil with residue removed, and (4) application of dye solution to a pre-wetted soil with residue removed and soil tilled by hand to a depth of 12 to 15 cm. Subplots were pre-wet by applying 20.0 cm of water over the plot and allowing redistribution of water to occur overnight. Brilliant Blue FCF, an anionic dye, was applied at a concentration of five g L<sup>-1</sup> to each of the subplots with a spray nozzle. A 4.0 cm depth of dye solution was applied at a constant rate of 6.8 cm hr<sup>-1</sup> to an effective plot diameter of 0.9 m. Approximately two hours after the application of the dye, the lower half of the circular plots were excavated to the depth of maximum dye penetration. Photographs of vertical cross-sections were taken to preserve a record of the dye patterns.

## Results and Discussion

### *Batch adsorption*

Adsorption isotherms for Brilliant Blue FCF (Fig. 1) were nonlinear and best described by a general Freundlich model (Kinniburgh et al. 1986). However, adsorption isotherms for Br<sup>-</sup> (Fig. 2) and NO<sub>3</sub><sup>-</sup> were linear within the range of concentrations considered in this study. Adsorption for all three anions increased with increasing soil depth. Distribution coefficients ( $K_d$ ) calculated from the slope of isotherms ranged from 0.0 to 1.7 L kg<sup>-1</sup> for Br<sup>-</sup> and 0.56 to 2.6 L kg<sup>-1</sup> for NO<sub>3</sub><sup>-</sup>. These values correspond to retardation factors ranging from 1.0 to 4.7 for Br<sup>-</sup> and 1.8 to 6.6 for NO<sub>3</sub><sup>-</sup>. Nitrate sorption was always greater than Br<sup>-</sup> sorption which suggests that NO<sub>3</sub><sup>-</sup> may be slightly more competitive than Br<sup>-</sup> in exchange reactions involving the displacement of Cl<sup>-</sup> in these soils. The ranges in distribution coefficients and retardation factors obtained in this study for NO<sub>3</sub><sup>-</sup> and Br<sup>-</sup> are, in general, somewhat higher than that reported for other Ultisols but fall within the range reported for Oxisols and Ultisols (Wong et al., 1990).

### *Displacement studies*

Concentrations predicted by the advective-dispersive equation agreed closely with the concentrations measured in the effluent at tensions greater than or equal to 10 cm of water corresponding to mean pore water velocities less than about 4.0 cm h<sup>-1</sup>. At higher mean pore water velocities, the fitted ADE generally provided a poor description of effluent concentrations at early and late times. Figure 3 shows the influence of mean pore water velocity on  $K_d/K_{deq}$  where  $K_d$  is the distribution coefficient obtained from the fit of the ADE to effluent concentrations at the corresponding pore water velocities. The variable  $K_{deq}$  represents the estimated equilibrium distribution coefficient for the same column at slow water velocities corresponding to tensions of 10 cm H<sub>2</sub>O or greater. The decrease in  $K_d/K_{deq}$  with increasing velocity indicates that local equilibrium between adsorbed and bulk solution concentrations was not attained as a result of slow diffusive exchanges between the macropore and matrix regions.

The dual-porosity model predicted large differences in transport between the surface (Ap/AB) and Bt2 horizons as evidenced by the plot of the predicted resident concentrations in each region as a function of time (Fig. 4). Obviously, the resident concentrations within the matrix region of the Bt2 horizon lag considerably behind the macropore concentrations. In contrast, the model fit obtained for the Ap/AB horizon at approximately the same pore water velocity demonstrates that both regions are nearly at equilibrium for all times. These results are in qualitative agreement with the thin sections prepared for these two horizons. For the Bt2 horizon, matrix regions are largely isolated

from large pores whereas for the Ap horizon, matrix regions are not isolated and located within a highly connective pore network (Fig. 5).

#### *Dye study*

Dye patterns exhibited by untilled subplots were characterized by the incomplete staining of the surface horizon and an accumulation of dye at and just below the interfacial area between the Ap and AB horizons (Figs. 6 and 7). This was typical of dye stained plots that were not tilled. In contrast, tilled plots (Fig. 8) exhibited rather uniform dye staining patterns with significantly ( $P < 0.05$ ) greater fraction of stained soil in the Ap horizon as compared to the subplots with residue intact. These results suggest that tillage decreased the degree of bypass flow in the surface horizon. At greater depths, all subplots exhibited stained regions that were associated with ped interfaces, roots and root channels.

#### **Conclusions**

Both batch and displacement experiments demonstrate that anion adsorption causes  $\text{Br}^-$  to move as much as four times slower than water in the subsoil. Under steady state flow conditions, diffusive exchanges between macropore and matrix regions were relatively rapid in the surface horizons. Accordingly, these results suggest that the effects of nonequilibrium upon solute transport in these horizons is negligible at steady state flow rates corresponding to expected rainfall intensities in the field (i.e. less than  $100 \text{ mm h}^{-1}$ ). In the Bt2 horizon, however, the dual-porosity model indicated that the rate of diffusive exchanges into and out of the matrix region, containing more than 95% of the soil water, was slow relative to the surface horizon.

The dye patterns exhibited in the surface horizons of this soil demonstrate that bypassing can occur under rainfall intensities far below that of saturated conductivity (approximately  $500 \text{ mm h}^{-1}$ ). The distinct flow paths in the surface horizon are likely a result of the initiation of wetting front instabilities generated just below the soil surface. In contrast to the column displacement experiments, the bypass flow exhibited in the Ap horizons of the dye stained plots may be important in controlling the mobility of solutes in the soils. The difference between these two studies lies in the fact that the dye tracer study was conducted under transient conditions corresponding to an infiltration event. Tillage was found to increase the interaction of the surface horizon with dye. Under no-till management, residence times of solute in undisturbed surface horizons would be expected to be longer than in tilled soils. This may be important when native sources of  $\text{NO}_3^-$ -N make significant contributions to crop requirements.

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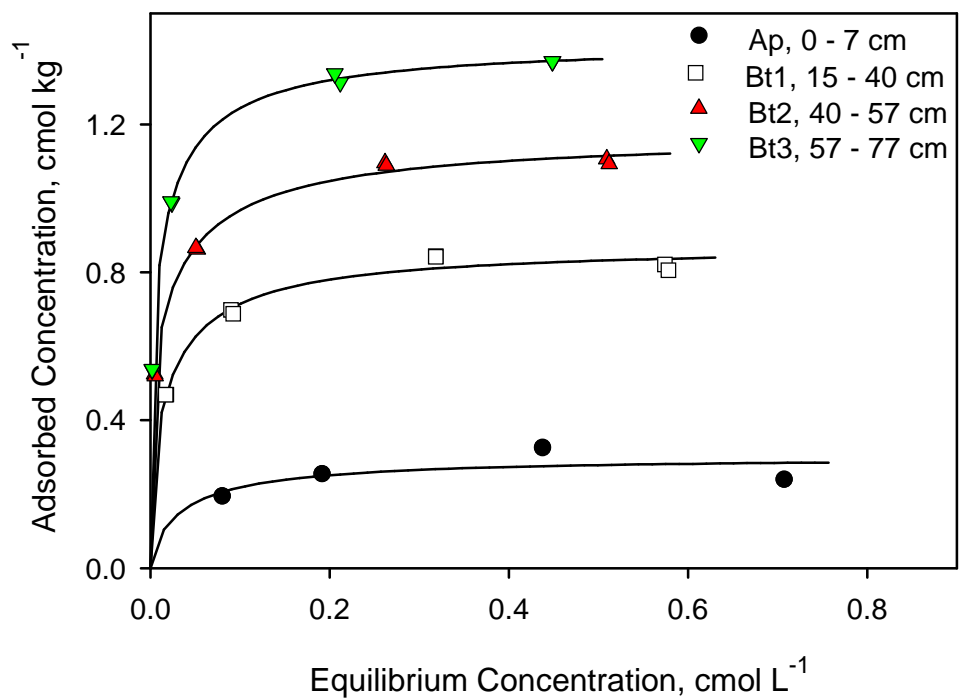


Fig. 1. Batch isotherms of Brilliant Blue FCF for several horizons of the CR2 pedon. The lines are the non-linear least squares fit of the general Freundlich isotherm to the data.

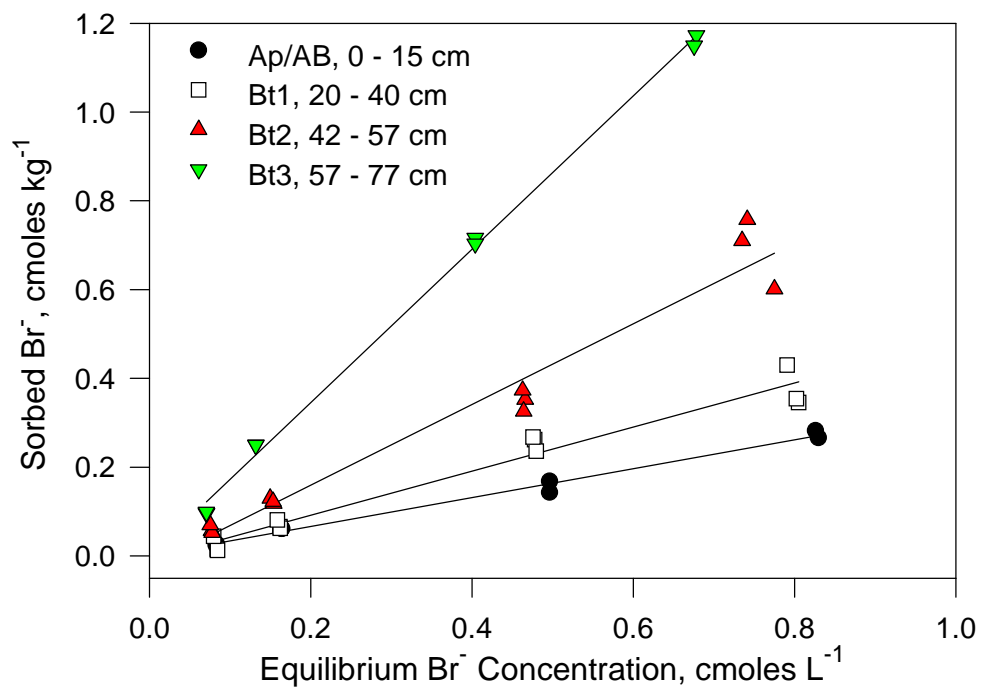


Fig. 2. Batch isotherms of bromide obtained for several soil samples in different horizons of the CR2 pedon. The lines are the least squares fit of the linear isotherm to the data.

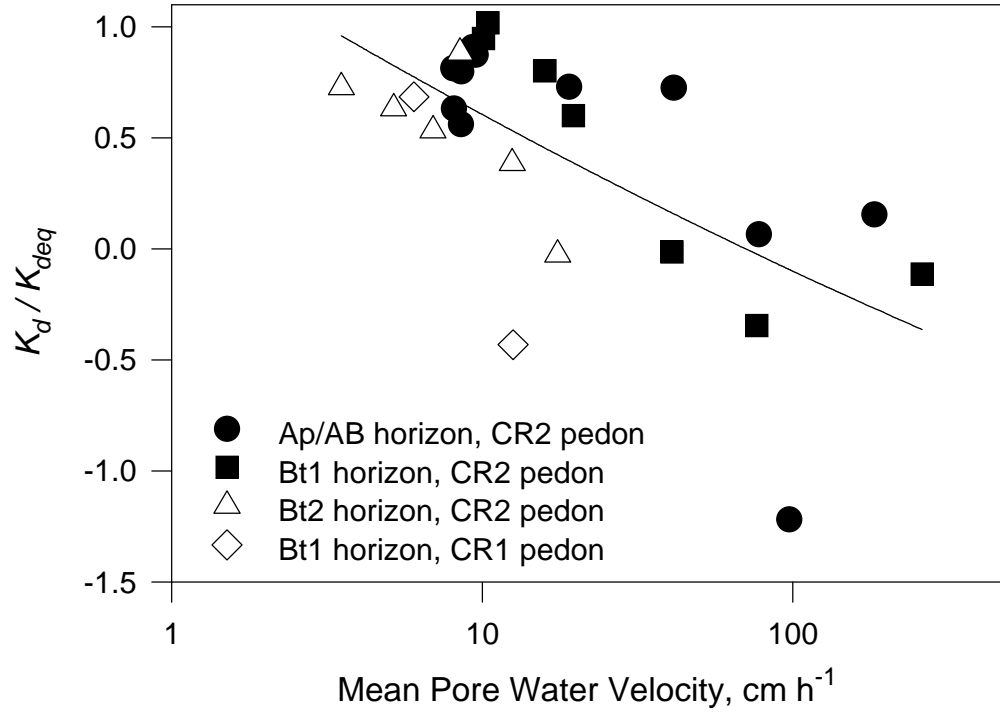


Fig. 3. Influence of the mean pore water velocity upon bromide adsorption  $K_d$  relative to equilibrium adsorption  $K_{deq}$  predicted by the ADE at slow ( $< 4 \text{ cm h}^{-1}$ ) pore water velocities.



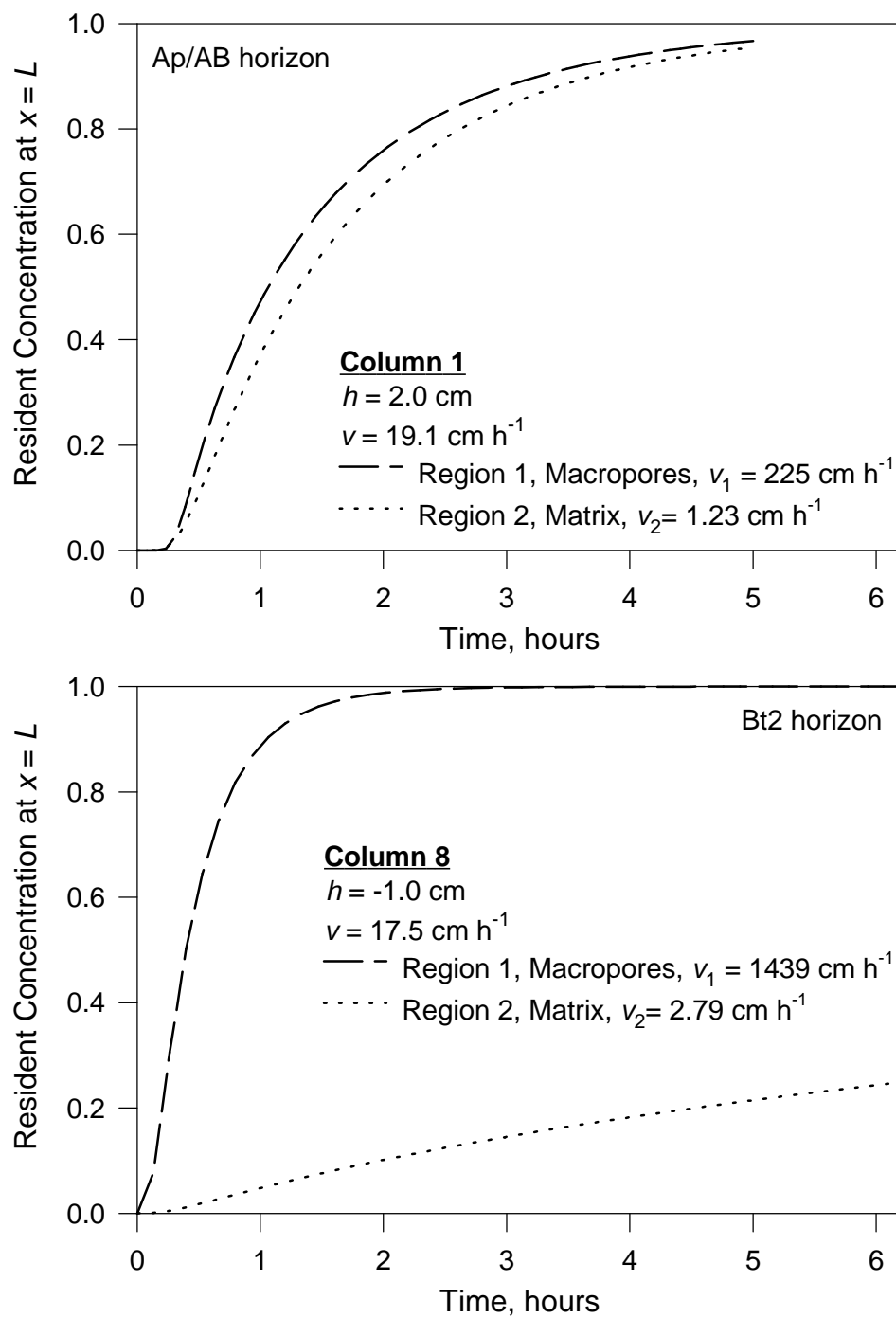


Fig. 4. Resident concentrations in the macropore and matrix regions predicted by the fit of the dual-porosity model to breakthrough curves for the Ap/AB and Bt2 horizons of the CR2 pedon.

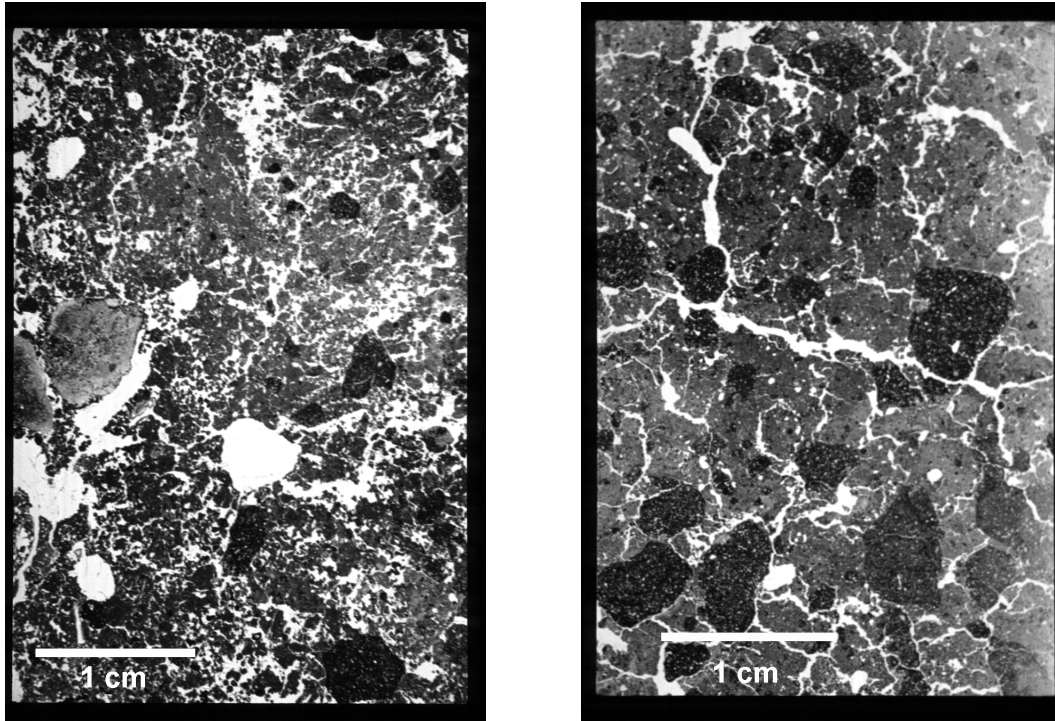


Fig. 5. Thin-sections of undisturbed peds for the Ap horizon (left) and the Bt2 horizon (right) of the CR2 pedon.

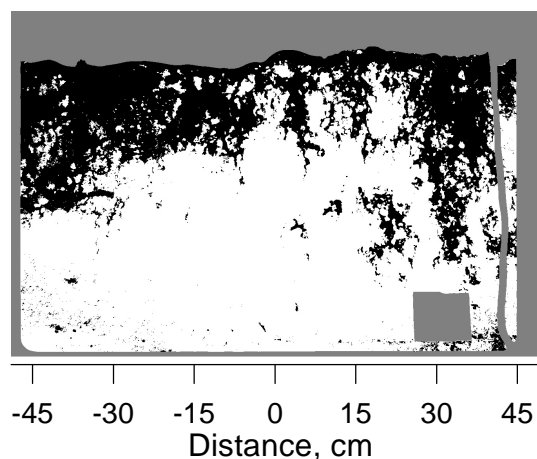


Fig. 6. Vertical cross-section of subplot with residue intact in plot B after a sprinkling application of 4.0 cm dye solution. Black areas are stained and gray areas in the image are labels or exterior regions.

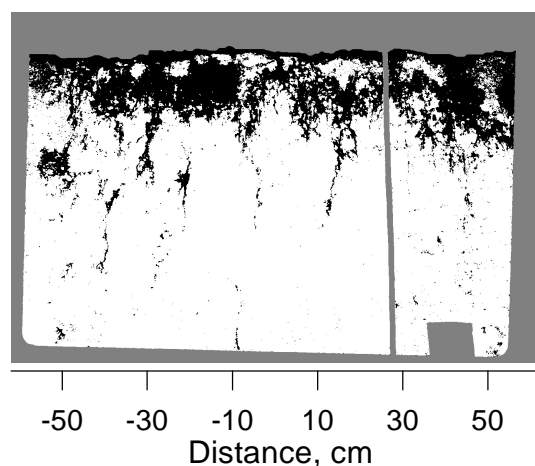


Fig. 7. Vertical cross-section of subplot with residue removed in plot B after a sprinkling application of 4.0 cm dye solution. Black areas are stained and gray areas in the image are labels or exterior regions. Image tilted to correct for slope.

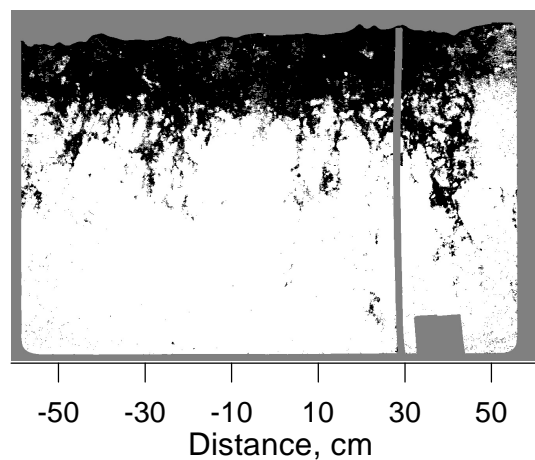


Fig. 8. Vertical cross-section of tilled subplot in plot B after a sprinkling application of 4.0 cm dye solution. Black areas are stained and gray areas in the image are labels or exterior regions.